Triterpenoids

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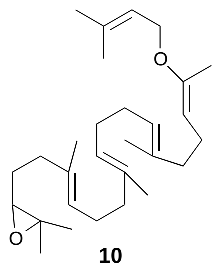
Covering: 1995
Previous review: 1996, 13, 151

1 Introduction

This article follows the pattern of the previous report. The use of triterpenoids as biomarkers in terrestrial and marine sediments,[1] the pharmacology of oleanolic and ursolic acids[2] and the biological activity of triterpenoids which show sweetness inhibition[3] have been reviewed.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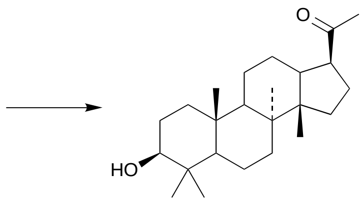
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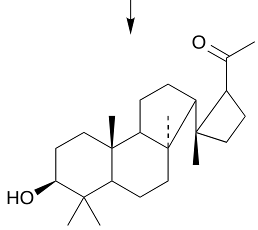
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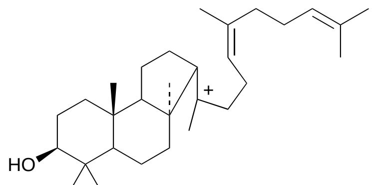
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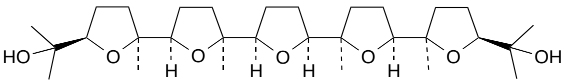
2 The squalene group

Glabrescol **1** is an interesting symmetrical squalene polytetrahydrofuran derivative from *Spathelia glabrescens*.[4] It is presumably derived from a squalene hexaepoxide. Enshuol **2** from *Laurencia omaezakiana*[5] and callicladol **3** from *L. calliclada*[6] must also arise from polyepoxysqualene precursors. Sapelin D **4** is a further oxygenated squalene from the bark of *Entandrophragma cylindricum*[7] (see *Nat. Prod. Rep.*, 1995, **12**, 609). A series of oxygenated squalenes has been isolated from *Quassia multiflora*.[8] Quassiol D **5** is a tetrol while quassiols B **6** and C **7** contain a tetrahydrofuran ring.

Sacridicene **8**, a monocyclic botryococcene, has been isolated from a lacustrine sediment deposited 10 280 years ago in Sacred Lake, Mount Kenya.[9] Octrahydrobotryococcene **9** has also been reported from sediments.[10]

The generally accepted concerted nature of the cyclisation of 2,3-oxidosqualene to lanosterol by lanosterol synthase from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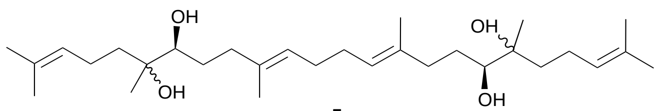
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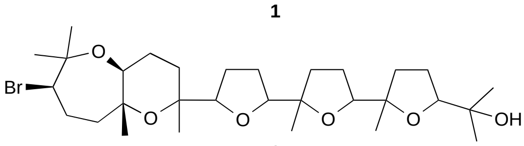
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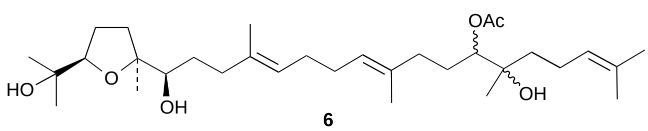
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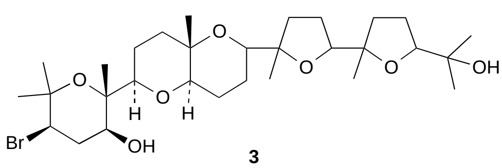
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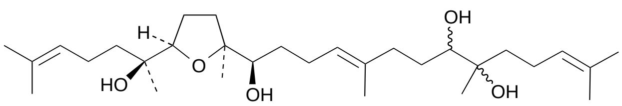
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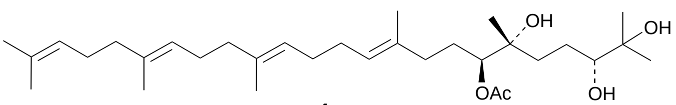
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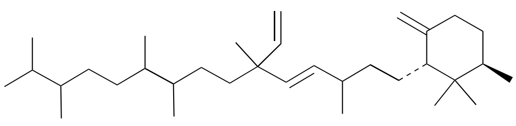
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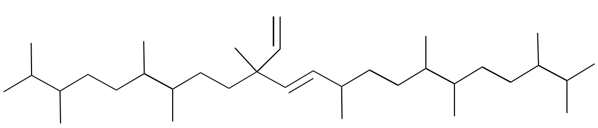
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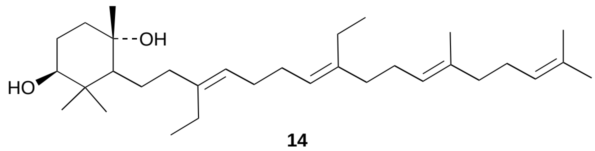
yeast has been challenged by Corey and his colleagues.[11] They argue that the formation of the minor product **11**, together with the expected product **12**, in the cyclisation of 20-oxa-2,3-oxidosqualene **10** suggests the intermediacy of discrete cations, like **13**, in the cyclisation of 2,3-oxidosqualene. (*S*)-2,3-Oxidosqualene has been prepared[12] from the corresponding 2-chloro-3-ketone by reduction with (*S*)-BINAL-H. Each of the (6*R*,7*R*)-, (6*S*,7*S*)-, (10*R*,11*R*)- and (10*S*,11*S*)-oxidosqualenes has been prepared and its absolute configurations determined.[13] Substitution of the methyl groups at C-10 and C-15 of 2,3-oxidosqualene with ethyl groups interferes with the normal cyclisation by the cyclase enzyme.[14] The reaction stops at the monocyclic stage with the formation of **14** and **15**. The former is a bis-homo achilleol A (see *Nat. Prod. Rep.*, 1994, **11**, 111).



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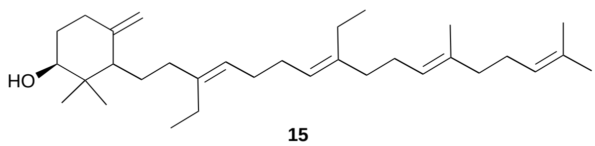

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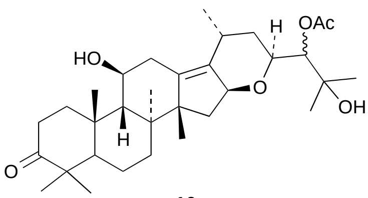
3 The fusidane–lanostane group

Alizexol A **16** is a novel protostane triterpenoid from the rhizomes of *Alisma orientalis*.[15] A rearranged lanostane, nigrum-24-en-3-one **17**, has been isolated from *Empetrum nigrum*[16] (the authors use a different numbering system, *i.e.* nigrum-21-en-3-one). Several crustinol derivatives, hebelomic acids B **18**, E **19** and F **20**, have been isolated from the mushroom *Hebeloma senescens*.[17] *Poria cocos* contains the trametenolic acid and dehydrotrametenolic acid derivatives **21**, **22** and **23**.[18] Other lanostanes from the same source include 3-epidehydrotumulosic acid **24**, the corresponding 25-hydroxy derivative **25**, and the ring A cleaved compounds poricoic acids B (as the methyl ester) **26**, E **27** and F **28**.[19] The highly oxygenated gonolactone A **29** is a metabolite of *Ganoderma lucidum*.[20] The 24,24-diethyllanostane *O*-methyllaureolol **30** has been isolated from *Skimmia laureola* subsp. *multinervia*.[21]



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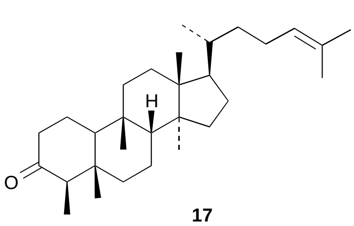

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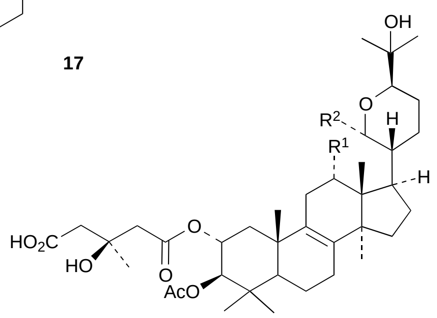
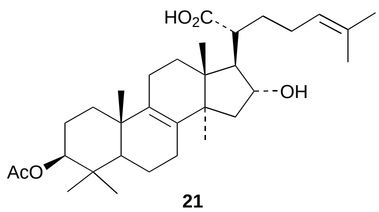


18 R^1 = OAc; R^2 = OH
19 R^1 = H; R^2 = OH
20 R^1 = H; R^2 = OAc



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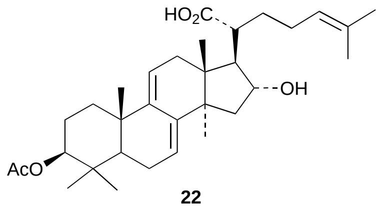

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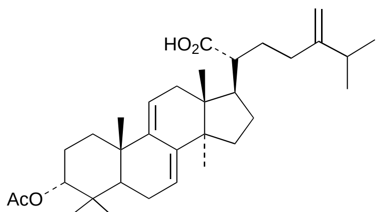

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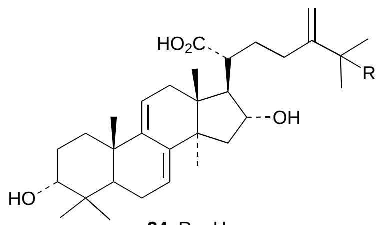
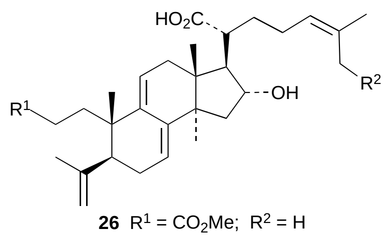
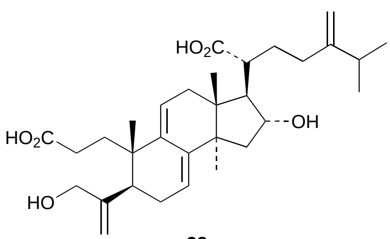


24 R = H
25 R = OH



26 R^1 = CO_2Me; R^2 = H
27 R^1 = CO_2H; R^2 = OH



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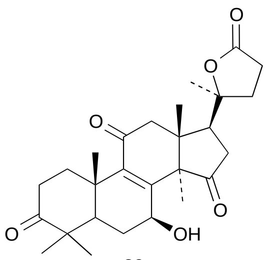

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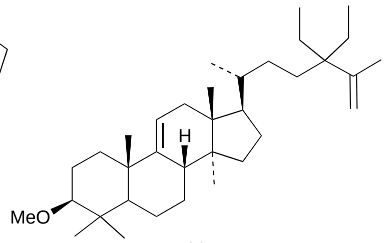

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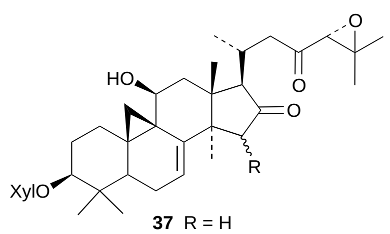
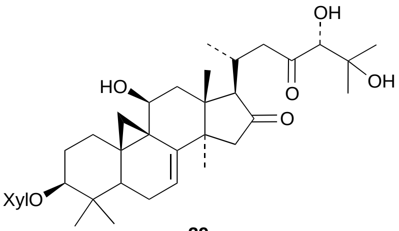


37 R = H
38 R = OH



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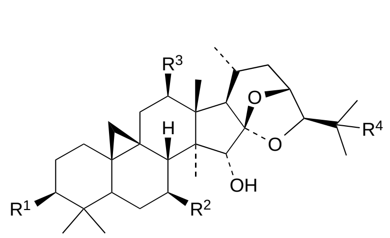
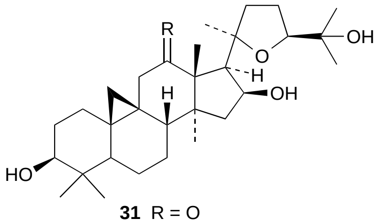
Experiments have shown that cycloartenol is not a precursor of lanosterol in *Euphorbia lathyrus*[22] while parkeol [lanost-9(11)-en-3β-ol] is a precursor of the holostane saponins in the sea cucumbers *Holothura florida* and *Actinopygia agassiza*.[23]

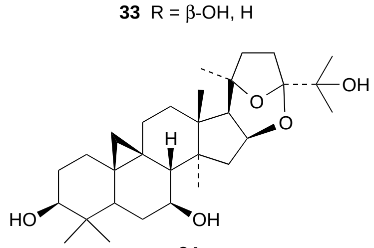
Three closely related cycloartanes, cycloalpigenins A **31**, B **32** and C **33** and their corresponding 3-*O*-β-D-xylopyranosides, cycloalpiosides A, B and C, have been isolated from *Astragalus alopecurus*.[24, 25, 26] Cycloalpigenin **34** and cycloalpioside, the corresponding 3β-D-xylopyranoside, are also present in *A. alopecurus*.[27] Two new glycosides **35** and **36** have been reported from *A. adsurgens*.[28] The saponins of several *Astragalus* species, *A. taschkendicus* (askendoside F)[29] *A. membranaceus* (astragalosides III and IV),[30] *A. trigonus* (trigonosides I–III),[31] *A. dissectus*, *A. ephemerotorum* and *A. kulabensis*,[32] have been reported.



40 R^1 = OXyl; R^2 = H; R^3 = R^4 = OH
41 R^1 = OArab; R^2 = H; R^3 = R^4 = OH
42 R^1 = OXyl; R^2 = OH; R^3 = H; R^4 = OH
43 R^1 = OXyl; R^2 = OH; R^3 = H; R^4 = OAc



31 R = O
32 R = α-OH, H
33 R = β-OH, H



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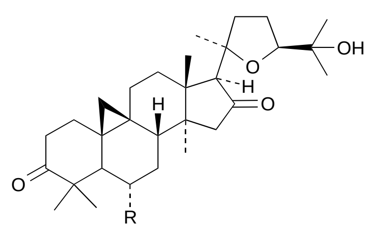
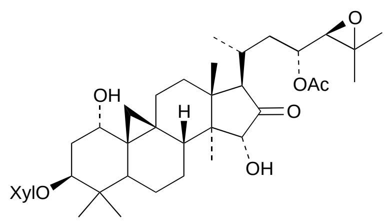


35 R = OGlc
36 R = OXyl



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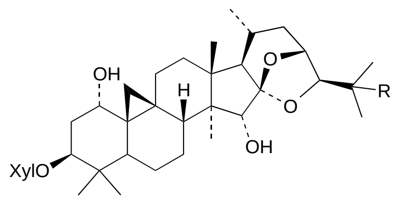
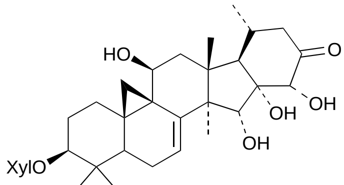


45 R = OH
46 R = OAc

Cimicifugosides H_1 **37**, H_2 **38** and H_5 **39** are new saponins from *Cimicifuga simplex*.[33] The genins are all new and that of cimicifugoside H_1 **37** was confirmed by X-ray analysis of the corresponding diacetate. Four new cimigenol derivatives **40**–**43** have been found in *C. simplex*[34] which also contains the 1α-hydroxyshengmanol derivative **44** and two further cimigenol derivatives **45** and **46**.[35] Full details of the isolation of cimicifugosides H_3 and H_4 (see *Nat. Prod. Rep.*, 1996, **13**, 153) have been reported[36] together with the new cimicifugoside H_6 **47**. Cimicifugosides H_4 and H_6 **47** have also been found in *C. foetida*[37] together with 25-anhydrocimigenol 3-*O*-β-D-xyloside **48**, cimicinol 3-*O*-β-D-xyloside **49**, cimicidanol **50**, cimicidanol 3-*O*-α-L-arabinoside **51**, cimicifol 3-*O*-β-D-xyloside **52**, cimicidol 3-*O*-β-D-xyloside **53** and the corresponding 15α-hydroxy derivative **54**, and the actein derivative **55**. Cimigenol 3-*O*-β-D-glucoside, cimiside F, also occurs in *C. foetida*.[38] The rhizomes of *Souliea vaginata* contain a range of cycloartane saponins, including a new compound, 26-deoxyactein **56**.[39]

Other cycloartanes include cycloart-24-ene-3β,16β,21-triol **57** from *Piptostygma fugax*,[40] 3β,28-dihydroxycycloartan-24-one **58** from *Aglaia harmsiana*[41] and the dimethyl ester of nigranoic acid **59** from *Tillandsia usneoides*.[42] The hydroperoxides **60** and **61** have been reported from *Tillandsia recurvata*.[43] *Murraya exotica* contains[44] the side-chain



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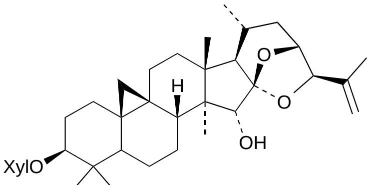

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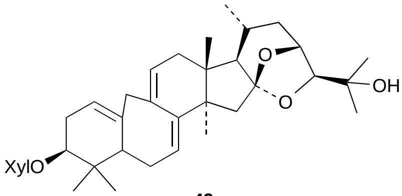

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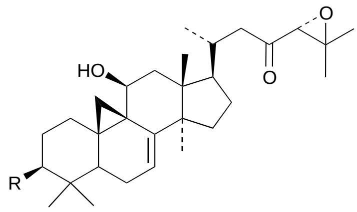
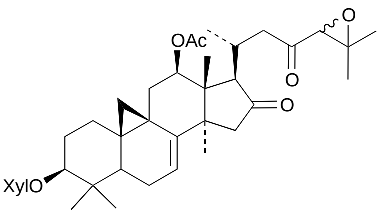


50 R = OH
51 R = OArab



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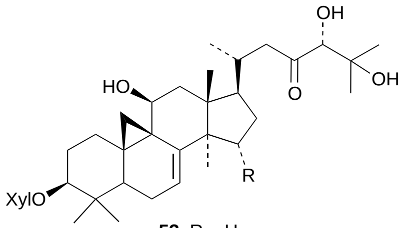
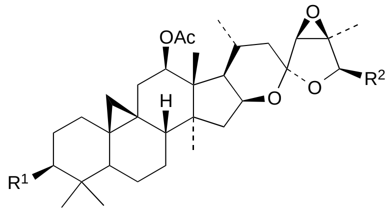
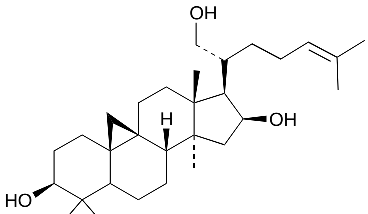


53 R = H
54 R = OH



55 R^1 = OArab; R^2 = OH
56 R^1 = OXyl; R^2 = H



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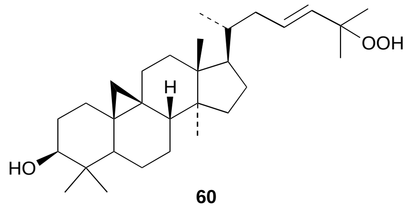

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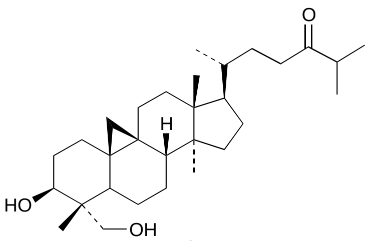

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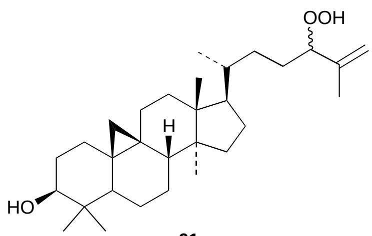

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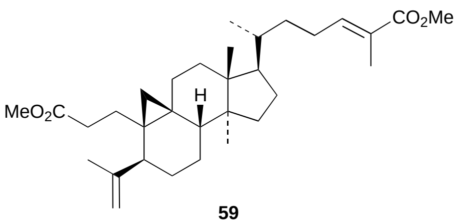

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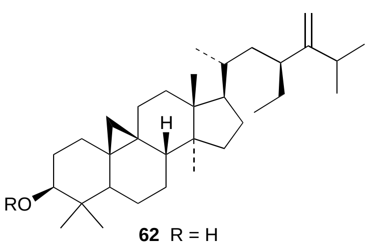
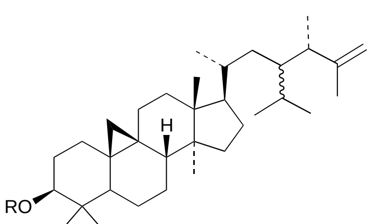


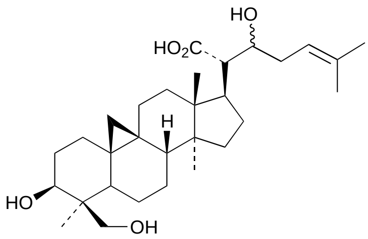
62 R = H
63 R = Me
64 R = Ac

alkylated derivatives **62**–**66**. Thalictosides V and IX, from *Thalictrum* species, are based on the new genin **67**.[45] Mussaendoside F from *Mussaenda pubescens*[46] is a further saponin based on heinsigenin A (see *Nat. Prod. Rep.*, 1994, **11**, 96).

Lovenone **68** is an interesting degraded cucurbitane derivative from *Adalaria loveni*.[47] *Caput nigri* is a rich source of cucurbitane glycosides. Capenosides D–L **69**–**77** have been isolated and characterised.[48, 49] The pharmacological effects of cucurbitacins have been reviewed.[50]



65 R = H
66 R = Ac



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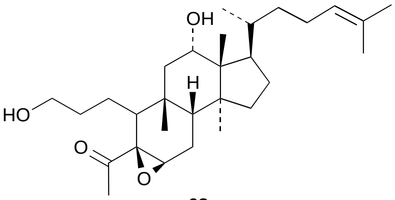

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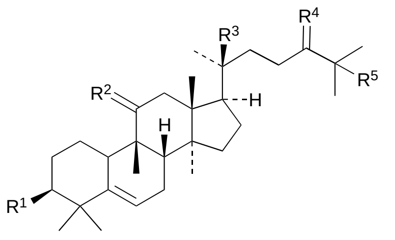
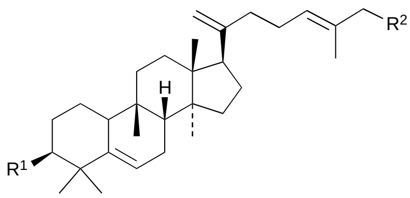


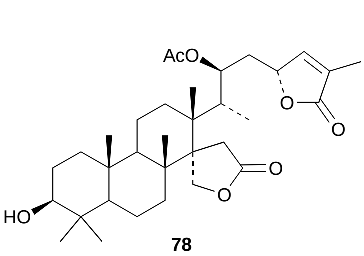
69 R^1 = GlcO; R^2 = O; R^3 = H; R^4 = OH,H; R^5 = OH
70 R^1 = GlcO; R^2 = α-OH,H; R^3 = H; R^4 = O; R^5 = GlcO
71 R^1 = Glc(1-2)GlcO; R^2 = α-OH,H; R^3 = H; R^4 = O; R^5 = GlcO
72 R^1 = Glc(1-6)GlcO; R^2 = α-OH,H; R^3 = H; R^4 = O; R^5 = GlcO
73 R^1 = Glc(1-6)GlcO; R^2 = O; R^3 = H; R^4 = O; R^5 = GlcO
74 R^1 = GlcO; R^2 = α-OH,H; R^3 = OH; R^4 = OH,H; R^5 = GlcO
75 R^1 = Glc(1-2)GlcO; R^2 = α-OH,H; R^3 = OH; R^4 = OH,H; R^5 = GlcO



76 R^1 = Glc(1-6)GlcO; R^2 = GlcO
77 R^1 = Glc(1-6)GlcO; R^2 = Glc(1-6)GlcO

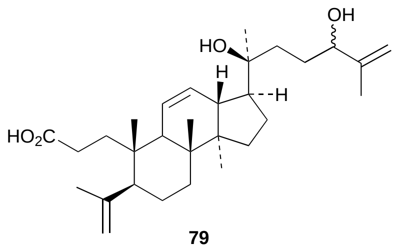
4 The dammarane–euphane group

Hovenidulcigenin A **78** is the genin of hovenidulciosides A_1 and A_2 from *Hovenia dulcis*.[51] The structure of hovenidulcigenin A **78** was confirmed by X-ray analysis and shown to be



78

a 16,17-secodammarane with a methyl migration from C-20 to C-17. Cyclocariosides II and III from *Cyclocarya paliurus* are the 24-*O*-α-L-arabinopyranoside of the 3,4-secodammarane **79** and the 12-*O*-β-D-quinovopyranoside of the 3,4-secodammarane **80**, respectively.[52] Several 25,26,27-trinordammaranes have been found in *Cleome amblyocarpa*;[53] they have



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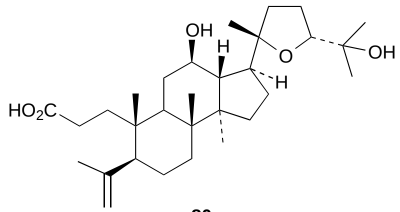

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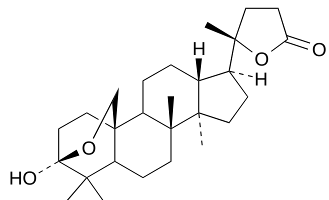
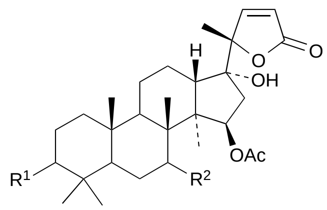
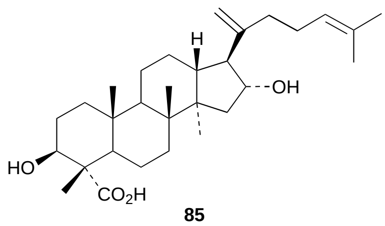


81



82 R^1 = β-OAc; R^2 = H
83 R^1 = R^2 = β-OAc
84 R^1 = α-OAc; R^2 = H



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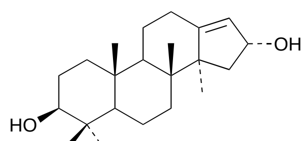

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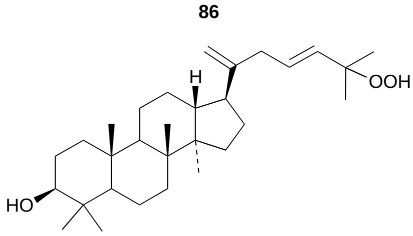

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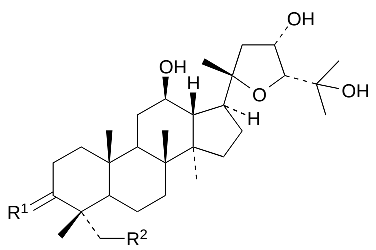
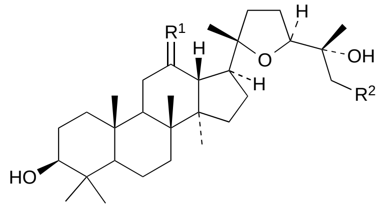
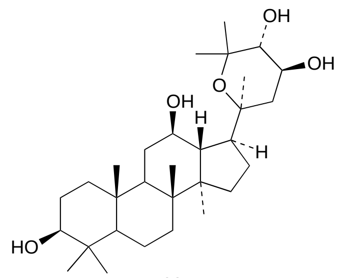


88 R^1 = O; R^2 = H
89 R^1 = β-OH,H; R^2 = OH



90 R^1 = O; R^2 = H
91 R^2 = H_2; R^2 = OH



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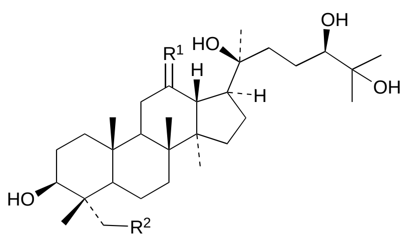
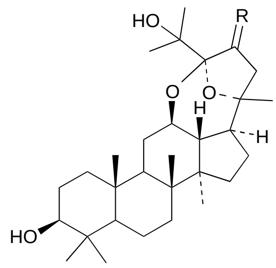
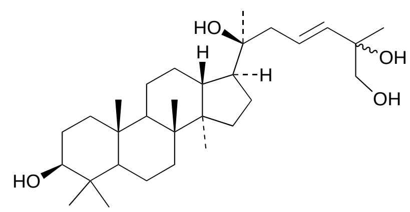


93 R^1 = H_2; R^2 = H
94 R^1 = β-OH,H; R^2 = H
95 R^1 = O; R^2 = H
96 R^1 = β-OH,H; R^2 = OH



97 R = β-OH, H
98 R = O



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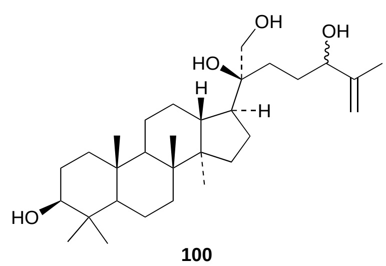

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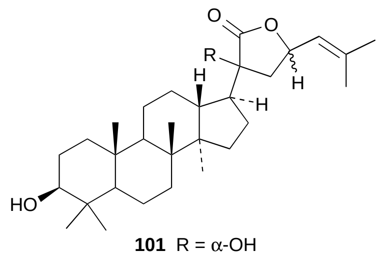
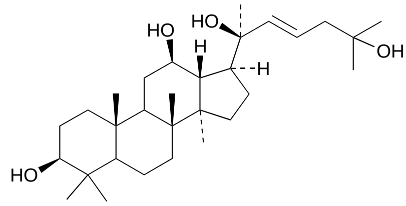


101 R = α-OH
102 R = β-OH



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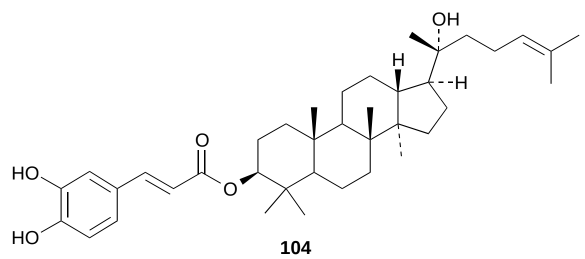
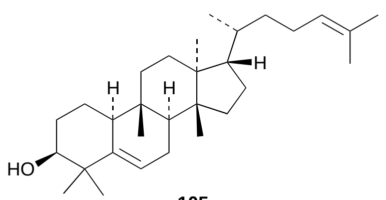


104

been named amblyone **81**, cleomblynols A **82** and B **83** and isocleomblynol A **84**. Rotundifolic acid from *Combretum rotundifolium* is the 16-*O*-α-L-arabinopyranoside of the new genin 3β,16α-dihydroxydammara-20,24-dien-28-oic acid **85**.[54] The 16-*O*-α-L-arabinopyranoside of the nordammarane 3β,16α-dihydroxymansumbin-13(17)-en-28-oic acid **86** is also found in the same plant. 25-Hydroperoxydammara-20,23-dien-3β-ol **87** has been isolated from *Boronia algida*.[55]

Neoalsomitra integrifoliola has produced 23 new saponins, the neoalsosides which include the new genins neolalsogenins B **88**, C **89**, G **90**, H **91**, M **92**, (20*S*,24*R*)-dammarane-3β,20,24,25-tetrol **93**, (20*S*,24*R*)-dammarane-3β,12β,20,24,25-pentol **94** and its 12-ketone **95**, (20*S*,24*R*)-dammarane-3β,12β,20,24,25,28-hexol **96** and the acetals **97** and **98**.[56, 57] The 20,24-diols **93–96** all readily cyclised to the corresponding 20,24-epoxides on acid treatment. Four saponins from *Gynostemma pentaphyllum* have the new genins dammar-23-ene-3β,20,25,26-tetrol **99**, dammar-25-ene-3β,20,21,24-tetrol **100** and the epimeric lactones **101** and **102**.[58] Koryoginsenosides R_1 and R_2 from *Panax ginseng* include the new genin dammar-22-ene-3β,12β,20,25-tetrol **103**.[59] Four dammarane saponins have been found in *Betula ermanii* together with the caffeate **104** of dammarenediol II.[60] Zizyotin is a saponin of jujubogenin from *Zizyphus oenoplea*[61] and another saponin of jujubogenin has been reported from *Centrosema bracteosum*.[62] Other new dammarane saponins with known genins include cyclocarioside I from *Cyclocarya paliurus*[63] and yixinoside A from *Gynostemma yixingense*.[64]

Boeticol **105** from *Euphorbia boetica* is 19(10→9)-*abeo*-eupha-5,24-dien-3β-ol.[65] The new tirucallane derivative leucophyllone **106** has been reported from *Aglaia leucophylla*,[66] and piscidinol B from *Walsura piscidia* has been shown to be identical with hispidol B **107**.[67] Dichapetalin A **108** is a glabretal analogue from *Dichapetalum madagascariense* with an unusual alkylation at C-3.[68] Another glabretal analogue **109** has been obtained from *Quassia multiflora*.[69] An X-ray analysis of cumingianoside A **110** has established the absolute configurations of cumingianosides A **110**, B, **111**, C **112**, D **113**, E **114** and F **115** from *Dysoxylum cumingianum*.[70]



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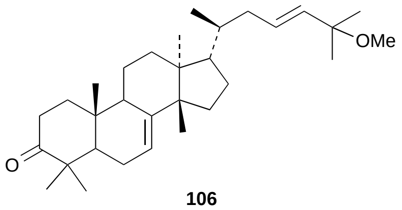

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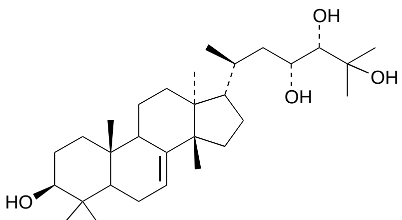

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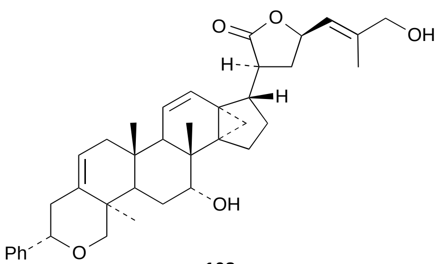

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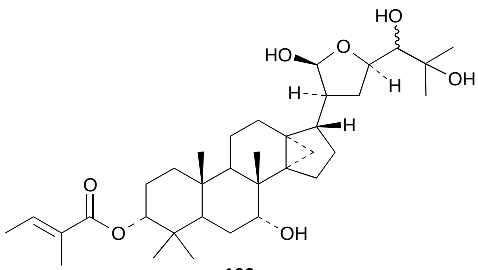

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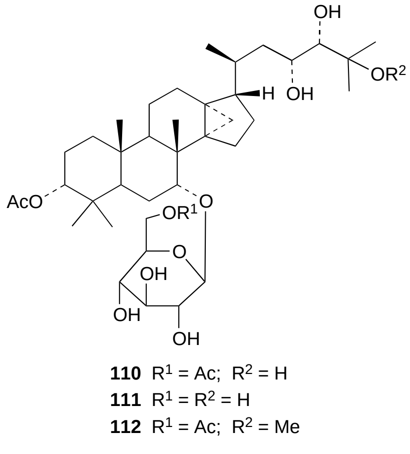
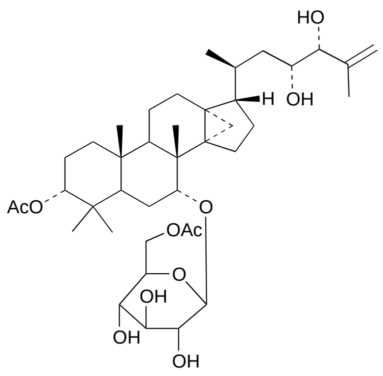


110 R^1 = Ac; R^2 = H
111 R^1 = R^2 = H
112 R^1 = Ac; R^2 = Me



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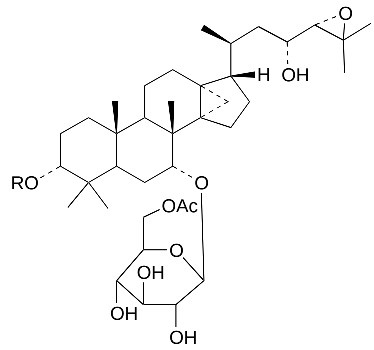
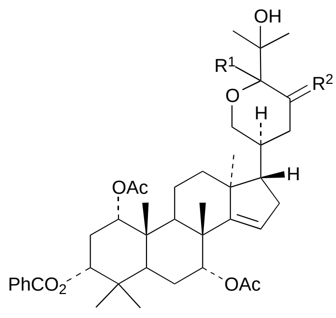
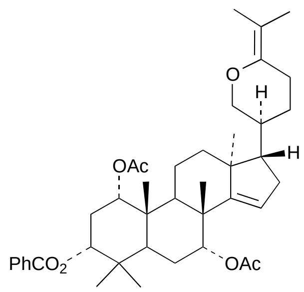


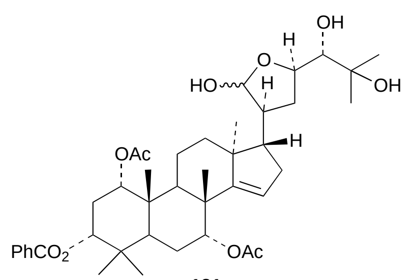
114 R = Ac
115 R = H



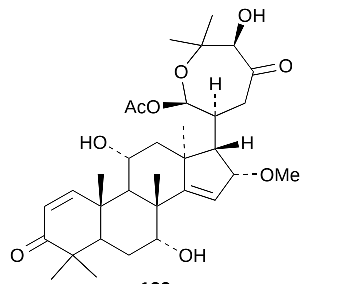
116 R^1 = OH; R^2 = α-OH, H
118 R^1 = α-H; R^2 = O
119 R^1 = α-OMe; R^2 = H_2
120 R^1 = β-OMe; R^2 = H_2



117

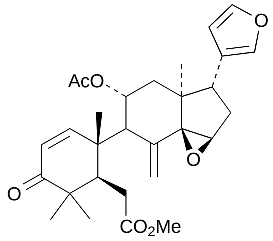


121



122

Several new apotirucallanes have been isolated from *Melia volkensii* including meliavolin **116**,[71] meliavolen **117**, melianinone **118**,[72] meliavolkensins A **119** and B **120**[73] and meliavolkenin **121**.[74] The structure of meliavolin **116** and the known melianin A[72] were confirmed by X-ray analysis. Piscicidol F **122** has been isolated from *Walsuria piscidia*.[67]



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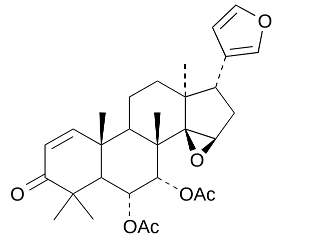

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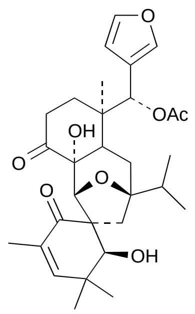
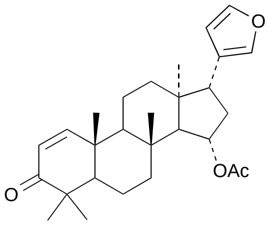
4.1 Tetranortriterpenoids

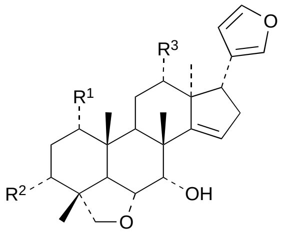
Structure **123** has been proposed for neeflene, a tetranortriterpenoid from the dried flowers of *Azadirachta indica*.[75] The lack of an oxygen substituent at C-7 is unusual. Trichilinins B **124**



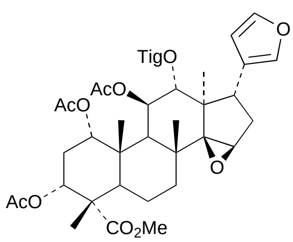
138



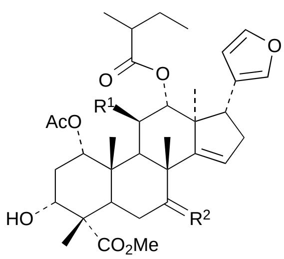
123



124 R^1 = OTig; R^2 = R^3 = OAc
125 R^1 = OAc; R^2 = OTig; R^3 = H
126 R^1 = OCin; R^2 = OAc; R^3 = H



127

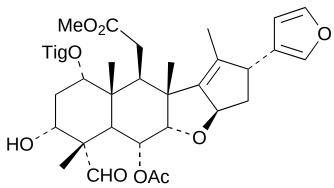


128 R^1 = OAc; R^2 = α-OAc,H
129 R^1 = OH; R^2 = α-OH,H
130 R^1 = OAc; R^2 = α-OH,H
131 R^1 = OAc; R^2 = O

and C **125** are constituents of *Melia toosendan*[76] and meliavolkin **126** is found in *M. volkensii*.[71] Further examples of the highly oxygenated tetranortriterpenoids from *Turraea* species have been reported. *T. nilotica* yielded nilotin **127**[77] while *T. floribunda* gave compounds **128–131**.[78]

New ring-A cleaved tetranortriterpenoids include rubralins A **132**, B **133** and C **134** from *Trichilia rubra*[79] and perforatinolone **135** from *Harrisonia perforata*.[80] 12-Deacetoxytoonacilin **136** occurs in *Toona ciliata* with the azadirone derivative **137**.[81] Entilin D **138** is a further example of the highly cleaved compounds from *Entandrophragma utile*.[82]

Further reports on the synthesis of azadirachtin[83] and the biologically active compounds from neem[84] have been



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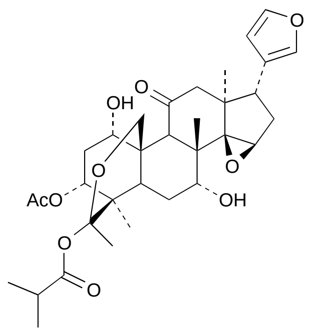

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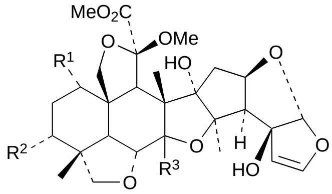
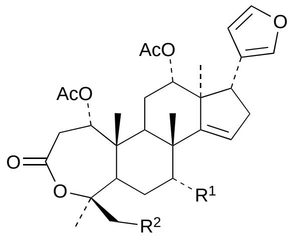
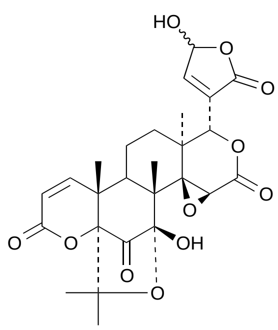


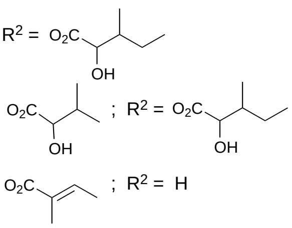
141 R^1 = OTig; R^2 = OAc; R^3 = α-H
142 R^1 = OAc; R^2 = OTig; R^3 = α-H
143 R^1 = H; R^2 = OTig; R^3 = β-H
144 R^1 = OAc; R^2 = OTig; R^3 = β-H
145 R^1 = OTig; R^2 = OAc; R^3 =β-H

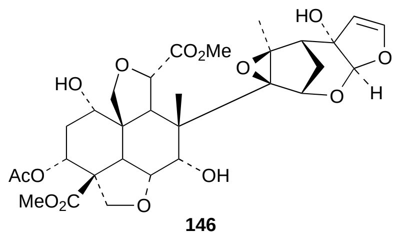




135

132 R^1 = R^2 =
133 R^1 = ; R^2 =
134 R^1 = ; R^2 = H





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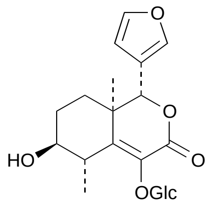

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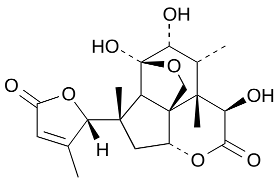
published. The flow of compounds from *Melia azedarach* continues. The latest additions are salannal **139**,[85] azedirachin C **140**[86] and the meliacarpinin derivatives **141** and **142**,[87] **143–145**[88] and the 1-desacylazadirachtin derivative **146**.[89] Fagaropsin **147** is a degraded limonoid from *Fagaropsis glabra*.[90]

4.2 Quassinoids

Polyandrol **148** is a C-19 quassinoid from *Castela polyandra*.[91] Other new quassinoids include bruceosides D **149**, E **150** and F **151** from *Brucea javanica*,[92] bruceanols G **152** and F **153** from *Brucea antidysenterica*,[93] and javanicin Z **154**, dihydrojavanicin Z **155** and hemiacetaljavanicin Z **156** from *Picrasma javanica*.[94] The structure of **156** was confirmed by X-ray analysis. Picrasinol D **157** is a constituent of *Picrasma ailanthoides*.[95]



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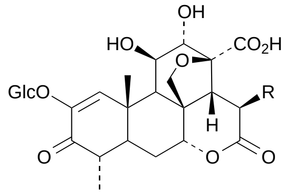
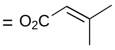
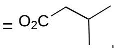
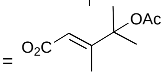
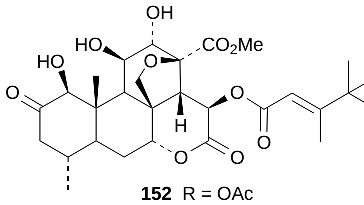


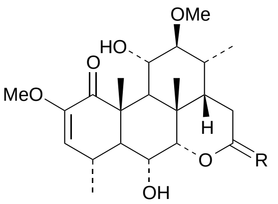
149 R = 

150 R = 

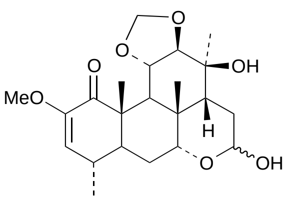
151 R = 



152 R = OAc
153 R = H



154 R = O
155 R = O ; 2β,3-dihydro
156 R = OH,H



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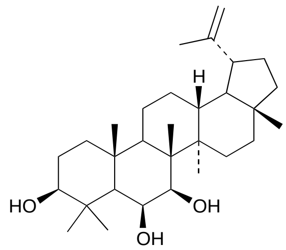

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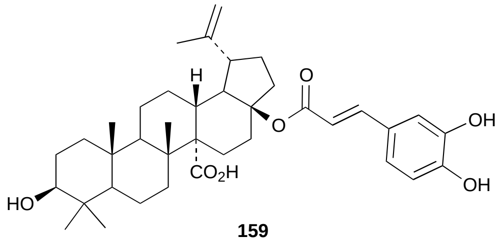

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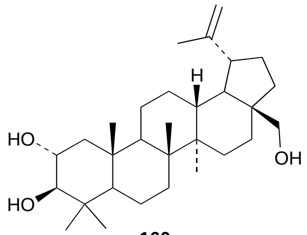

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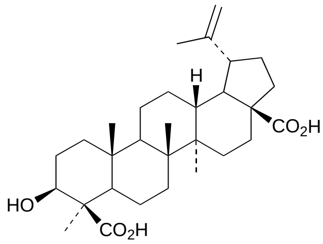

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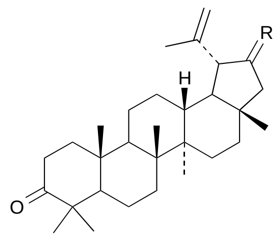
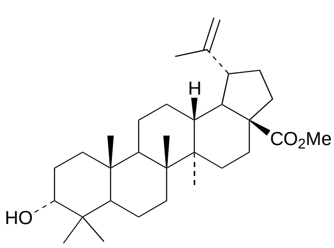


163 R = O
164 R = β-OH, H



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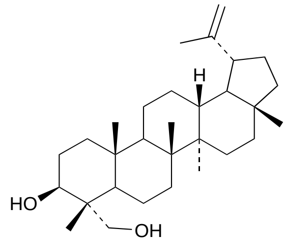


165

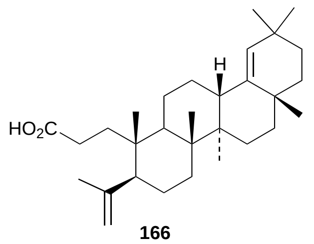
5 The lupane group

Two new lupane derivatives, the 3β,6β,7β-triol **158** and the rare 27-carboxylic acid **159**, have been isolated from *Rhoiptelea chiliantha*.[96] The 2α,3β,28-triol **160** and the corresponding 3,28-dipalmitate have been found in *Rheum rhabarbium*.[97] Other new lupanes include 3β-hydroxylup-20(29)-ene-24,28-dioic acid **161** from *Mimusops elengi*,[98] methyl 3-*epi*-betulinate **162** from *Syzygium samarangense*,[99] salacianone **163** and salacianol **164** from *Salacia beddomei*,[100] lup-20(29)-ene-3β,23-diol **165** from *Bursera simaruba*[101] and lupeol caffeate from *Betula ermanii*.[60]

Three lupane glycosyl esters, oplopanaxosides B, C and D, have been isolated from the leaves of *Oplopanax japonicus*[102] and have been shown to be saponins of 3β-hydroxylup-20(29)-ene-23,28-dioic acid, 3α,23-dihydroxylup-20(29)-en-28-oic acid and 3β,23-dihydroxylup-20(29)-en-28-oic acid, respectively. These saponins have previously been published as the cirensosides F, H and G, respectively.[103] A lupane saponin has been reported from *Coccinia indica*.[104]

6 The oleanane group

3,4-Secooleana-4(23),18-dien-3-oic acid **166** has been found in *Vahlia capensis*[105] while the 2,3-secooleanane dillenic acid D **167** has been isolated from *Dillenia papuana* together with dillenic acid E **168** and 3-oxoolean-12-en-30-oic acid **169**.[106] 1β-Hydroxy-3-oxoolean-12-en-28-oic acid **170** has been detected in *Limnophila rugosa* and 28-hydroxyolean-13(18)-en-3-one **171**, named sabianone, has been found in *Sabinia*



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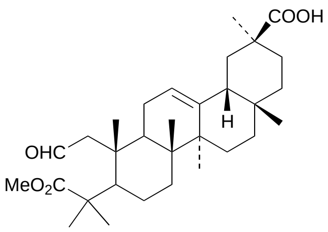

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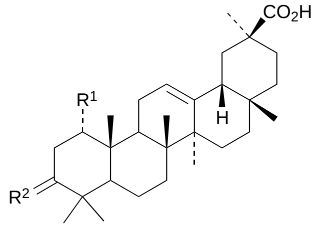
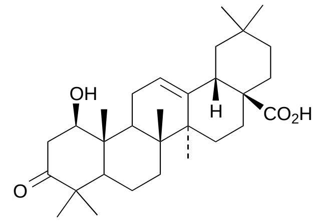


168 R^1 = OH; R^2 = β-OH,H
169 R^1 = H; R^2 = O



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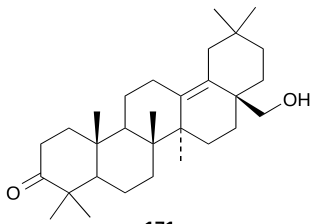

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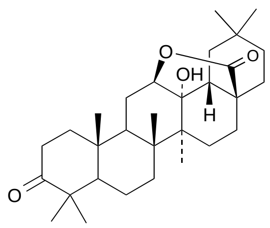

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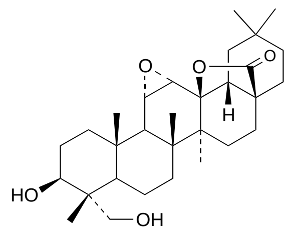

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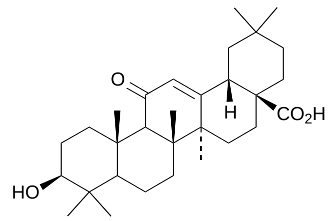

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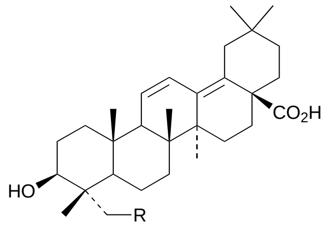
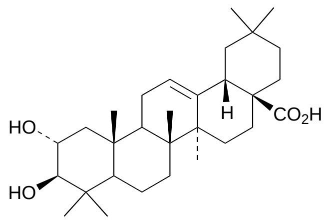


175 R = H
176 R = OH



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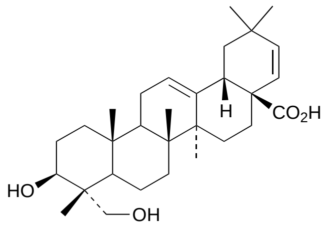

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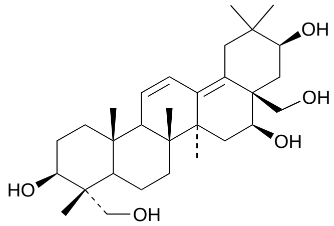

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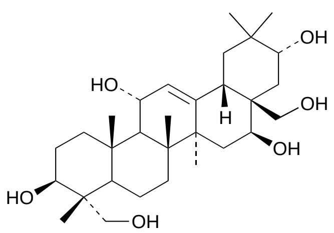

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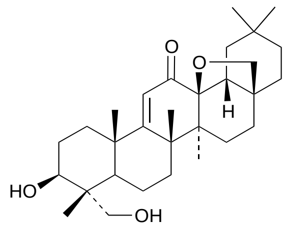

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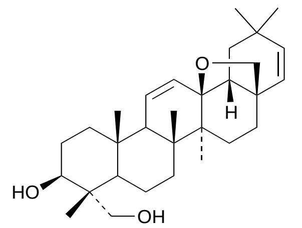

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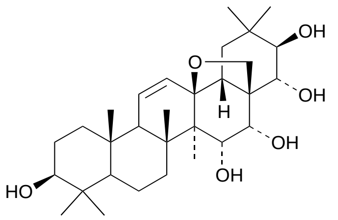

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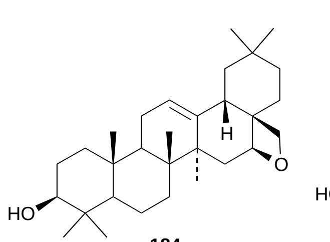

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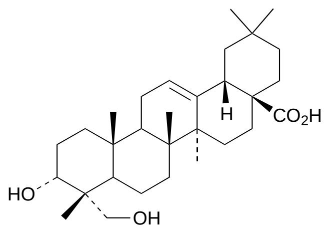

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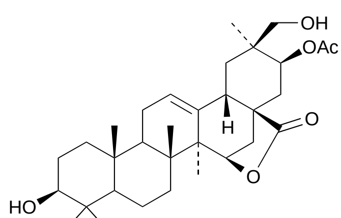

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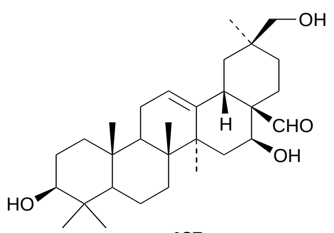

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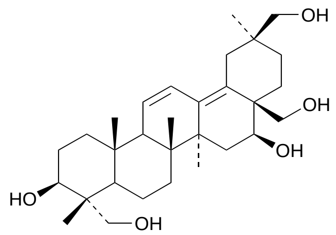

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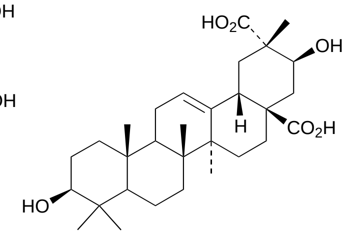

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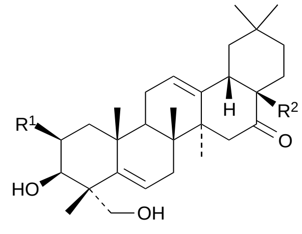
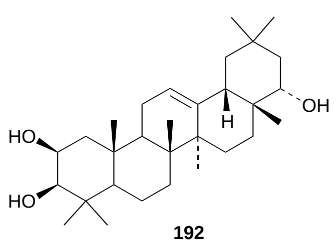


190 R^1 = OH; R^2 = H
191 R^1 = H; R^2 = CH_3



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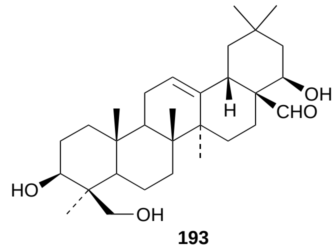

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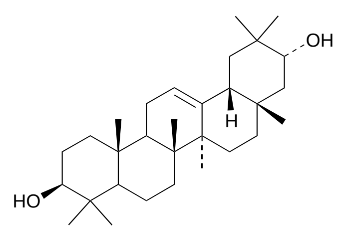
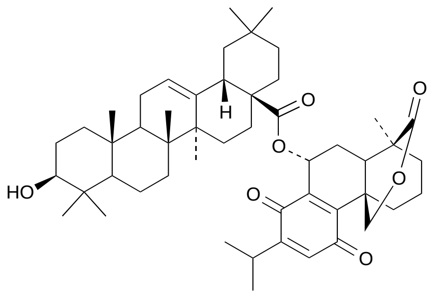


194

swinhoei, together with sabialactone **172**.[107] *Paeonia japonica* is the source of 3β,23-dihydroxy-11α,12α-epoxyoleanan-28,13β-olide **173**, 3β-hydroxy-11-oxoolean-12-en-28-oic acid **174** and 3β-hydroxyoleana-11,13(18)-dien-28-oic acid **175** whereas the corresponding 23-hydroxy derivative **176** and 2α,3β-dihydroxyolean-12-en-28-oic **177** are found in *Paeonia suffruticosa*.[108] The clinopodisides B–G are saponins from *Clinopodium chinensis* with the new sapogenins 3β,23-dihydroxyoleana-12,21-dien-28-oic acid **178**, oleana-11,13(18)-diene-3β,16β,21β,23,28-pentol **179**, olean-12-ene 3β,11α,16β,21α,23,28-hexol **180**, the 13β,28-epoxyoleananes **181** and **182**.[109] 13β,28-Epoxyolean-11-ene-3β,15α,16α,21β,22α-pentol **183** is the genin of the new saponin ranuncoside VII from *Hydrocotyle ranunculoides*.[110] Liguveitol **184**, the unusual 16β,28-epoxyolean-12-en-3β-ol, is the genin of liguveitoside A from *Ligularia veitchiana*.[111] Other new oleananes include wilforol C **185**, the 3-epimer of hederagenin from *Tripterygium wilfordii*,[112] bridgesigenin C **186** from *Trichocereus pachanoi*,[113] alamosenogenin **187** from *Rathbunia alamosensis*,[114] oleana-11,13(18)-diene-3β,16β,23,28,30-pentol, saikaogenin Q **188**, the genin of saikosaponin Q from *Bupleurum smithii* va. *parvifolium*,[115] philoxeroic acid **189** from *Alternanthera philoxeroides*,[116] mimusopgenone **190** and mimugenone **191** from *Mimusops elengi*,[117] olean-12-ene-2β,3β,22α-triol **192** from *Picris hieracioides*,[118] 3β,22β,24-trihydroxyolean-12-en-28-al **193**, the genin of lablabsaponin I from *Dolichos lablab*[119] and glyyunnansapogenin **194** from *Glycyrrhiza yunnanensis*.[120]

Reglin **195** from *Salvia regla* is an ester of oleanolic acid and the abietane deacetylsessein which both occur in the plant.[121] Other new naturally occurring oleanane esters include methyl 3α-hydroxyolean-18-en-28-oate **196** from a *Frullania* sp.,[122] methyl 3-benzoylkatonoate **197** from *Limnophila heterophylla*,[123] the bis-caffeoyl ester **198** of 3β,27-dihydroxyolean-12-en-28-oic acid from *Rhoiptelea chiliantha*,[96] camarilic acid **199**[124] and camaric acid **200**[125] from *Lantana camara* and 3-coumaroylarjunolic acid **201** from *Myrianthus liberecus*.[126]



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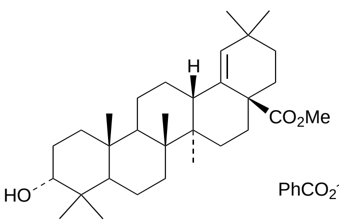

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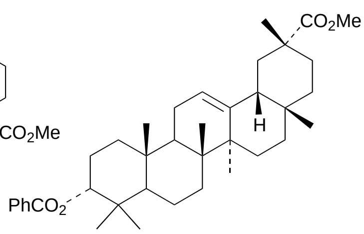

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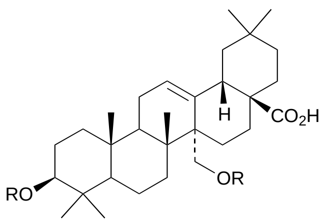

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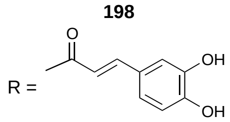
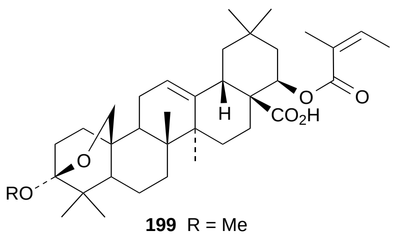
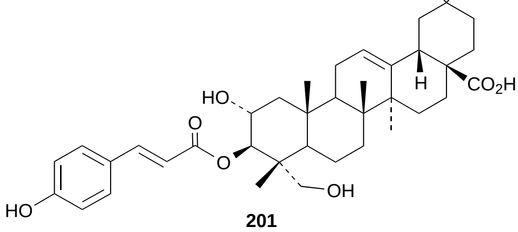




199 R = Me
200 R = H



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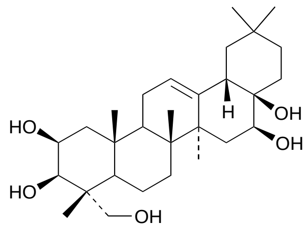

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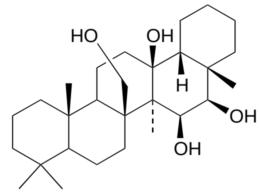
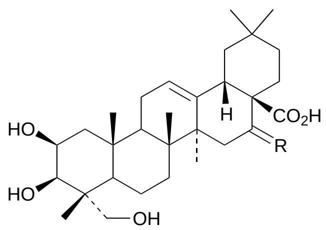
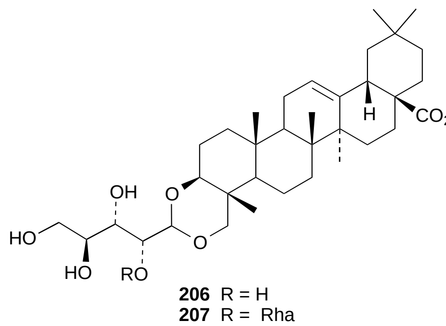


203

Vicogenin **202** is a 28-nororleanane from *Vicoa indica*[127] and the unusual 29,30-dinoroleanane-13β,15β,16β,26-tetrol **203** has been found in the soft coral *Nephthea albida*.[128] A full assignment of the ^{1}H and ^{13}C NMR spectra of the 27-noroleanane pyrocincholic acid has been reported.[129] Bernardioside B_4 is a new saponin from *Bellis bernardii* along with the new sapogenin bellisonic acid **204**.[130] The polygalasaponins XI–XIV from *Polygala japonica* include a new genin named polygalagenin **205**.[131] Anemoclemosides A **206**



204 R = O
205 R = H_2



206 R = H
207 R = Rha

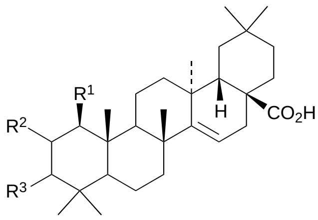
Table 1 New oleanane saponins

Compound(s)	Source	Ref.
Achyranthosides C and D	*Achyranthes fauriei*	133
Albiziasaponins A, B and C	*Albizia lebbeck*	134
Aradecoside	*Aralia decaisneana*	135
Armatoside	*Aralia armata*	136
Asterbatanosides D and E	*Aster batangensis*	137
Asterbatanosides F, G, H and I	*Aster batangensis*	138
Asterbat anosides J and K	*Aster batangensis*	139,140
Asteryunnanosides A, B, C and D	*Aster yunnanensis*	141,142
Asteryunnanoside E	*Aster yunnanensis*	143
Asteryunnanosides F and G	*Aster yunnanensis*	144
Asteryunnanoside H	*Aster yunnanensis*	145
Bellidiastroside C_2	*Aster bellidiastrum*	146
Bersimosides I and II	*Trifolium alexandrinum*	147
Betavulgarosides I–V	*Beta vulgaris*	148
Cephalariasaponin B	*Cephalaria transsylvanica*	149
Clematichinensosides A and B	*Clematis chinensis*	150
Clematosides A–G	*Clematis stans*	151
Clemontanoside E	*Clematis montana*	152
Elatosides G–K	*Aralia elata*	153
Esculentosides L_1 and R	*Phytolacca acinosa*	154
2′-*O*-β-D-Glucopyranosylmomordins Ic and IIc	*Kochia scoparia*	155
Glycoside L-6d	*Hedera helix*	156
Hacquetia saponins 1–4	*Hacquetia epipactis*	157
Herniaria saponin A	*Herniaria fontanesii*	158
Inflasaponins II and VI	*Glycyrrhiza inflata*	159
Japondipsaponin E_1	*Dipsacus japonicus*	160
Kalopanaxsaponins G and H	*Kalopanax sepemlobus*	161
Kudzusaponins SA_1–SA_3 and C_1	*Pueraria lobata*	162
Linderniosides A and B	*Lindernia pyxidaria*	163
Lucyoside O	*Luffa cylindrica*	164
Lucyoside P	*Luffa cylindrica*	165
Mazusaponins I and III	*Mazus miquelii*	166
Melilotosides A–C	*Melilotus albus*	167
Melilotoside D	*Melilotus albus*	168
Mimusopin and Mimusopsin	*Mimusops elengi*	169
Mussaendoside S	*Mussaenda pubescens*	170
Patensin	*Pulsatilla patens* var. *multifida*	171
Polyandrasides A and B	*Phytolacca polyandra*	172
Polygalasaponins I–X	*Polygala japonica*	173
Reiniosides A–F	*Polygala reinii*	174
Rubicunoside A	*Silene rubicunda*	175
Saikosapons M and N	*Bupleurum smithii*	176
Saponins E3, E6–E8	*Ilex dumosa*	177
(*E*)- and (*Z*)-Senegasaponins A and B, (*Z*)-Senegins II and III	*Polygala senega* var. *latifolia*	178,179
Sideroxylosides B and C	*Sideroxylon foetidissimum*	180
Songarosaponins E and F	*Verbascum songaricum*	181
Symphytoxide B	*Symphytum officinale*	182
Tauroside St-I_2	*Hedera taurica*	183
Terminolitin	*Terminalia arjuna*	184
Thalicoside D	*Thalictrum minus*	185
Transsylvanosides E and F	*Cephalaria transsilvanica*	186
Trifosides A–C	*Akebia trifoliata*	187
Wistariasaponins A_2, A_3, B_3, YC_1 and YC_2	*Wisteria brachybotrys*	188
Yiyeliangwanosides VII and VIII	*Nothopanax davidii*	189
Yiyeliangwanosides IX–XI	*Nothopanax davidii*	190

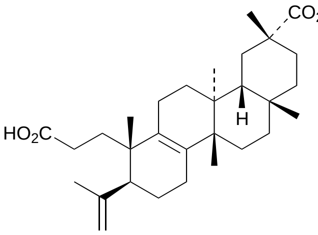
and B **207** are saponins from *Anemoclema glaucifolium* with an unusually linked arabinose.[132] Other named oleanane saponins with known genins are listed in Table 1.

The following plant sources have been reported to contain unnamed saponins of known oleanane genins: *Alalia armata*,[191] *Catunaregam nilotica*,[192] *Dumasia truncata*,[193] *Enterospermum pruinosum*,[194] *Gypsophila capillaris*,[195] *Gypsophila oldhamiana*,[196] *Mimosa pigra*,[197] *Myrsine australis*,[198] *Phytolacca rivinoides* and *Phytolacca bogotensis*,[199] *Pometia eximia*,[200] *Silene jenisseensis*,[201] *Solidago virgaurea* subsp. *virgaurea*,[202] *Sophora japonica*[203] and *Vigna unguiculata* subsp. *unguiculata*.[204]

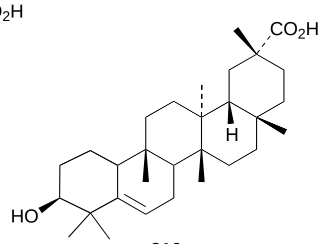
A host of taraxerane derivatives has been isolated from *Maprounea africana* and *M. membrancea*.[205, 206] These include the *p*-coumaroyl ester **208** of aleuritolic acid, the 2α-hydroxy- **209** and 2β-hydroxy-3-epialeuritolic acid **210**, the 2,3-bis-(*p*-hydroxybenzoyl) ester of 1β,2α-dihydroxyaleuritolic acid **211** and the 3-(*p*-hydroxybenzoyl) esters of 2α-hydroxyaleuritolic acid **212** and 1β-hydroxyaleuritolic acid **213**. The last named ester was previously thought to be an ester of 7β-hydroxymaprounic acid. The X-ray crystal structure analysis of the known bryononic acid has been reported.[207] Bryononic acid was found in *Sandoricum koetjape* together with secobryononic acid **214** and the corresponding Δ^7-isomer, secoisobryononic



208 $R^1 = R^2 = H$; R^3 = β-coumaroyloxy
209 $R^1 = H$; R^3 = β-OH; R^2 = α-*p*-hydroxybenzoyloxy
210 $R^1 = H$; R^2 = β-*p*-hydroxybenzoyloxy ; R^3 = α-OH
211 R^1 = OH; R^2 = α-*p*-hydroxybenzoyloxy; R^3 = β-*p*-hydroxybenzoyloxy
212 $R^1 = H$; R^2 = α-OH; R^3 = β-*p*-hydroxybenzoyloxy
213 R^1 = OH; $R^2 = H$; R^3 = β-*p*-hydroxybenzoyloxy



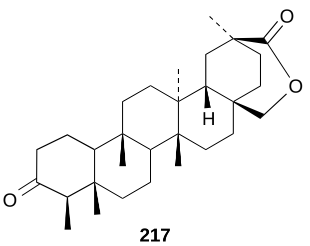
214
215 Δ^7 isomer



216

acid **215**. Wilforol D **216** is a glutinane derivative from *Trypterigium wilfordii*.[112]

Several friedelane derivatives have been isolated from *Maytenus* species including maytenfolone **217** from *M. diversifolia*,[208] 2α-hydroxy-3-oxofriedelan-29-oic acid **218**, 16β-hydroxyiguesterin **219**,[209] canarol **220**, 7α-hydroxycanarol **221**, 7α-hydroxy-6-oxo-7,8-didehydroiguesterol **222**, canarodial **223**, iguesteroquinone **224** and 7α-hydroxy-7,8-dihydroiguesterin **225** from *M. caniariensis* and blepharodol **226** and 7α-hydroxyblepharodol **227** from *M. blepharodes*.[210] The dimeric friedelane derivatives xuxuarine Aα **228**, Aβ **229**, Bα **230**, Bβ **231**, Cα **232**, Cβ **233**, Dα **234** and Dβ **235** and 7′,8′-dihydroxuxuarine Aβ **236** have been isolated from *M. chuchuhuasca*.[211] Wilforol A **237**, a norfriedelane derivative,



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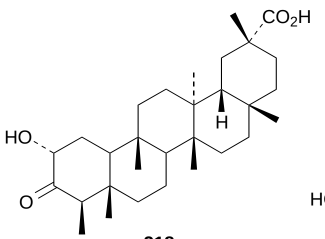

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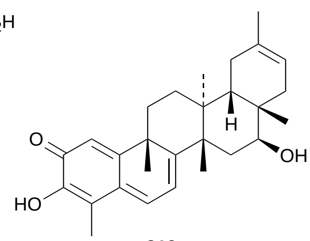

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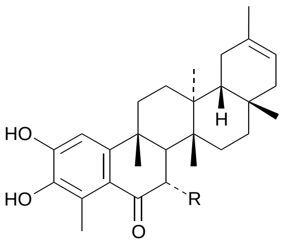
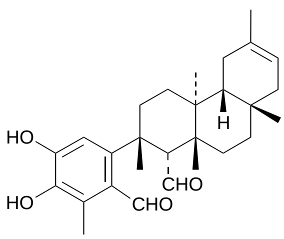


220 R = H
221 R = OH
222 R = OH; 7,8-didehydro



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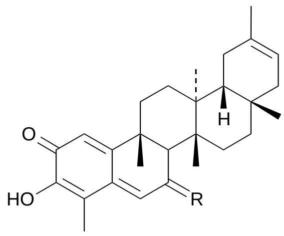
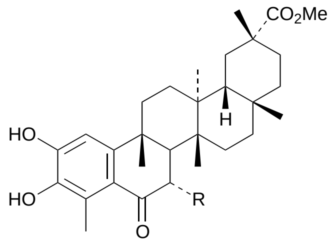
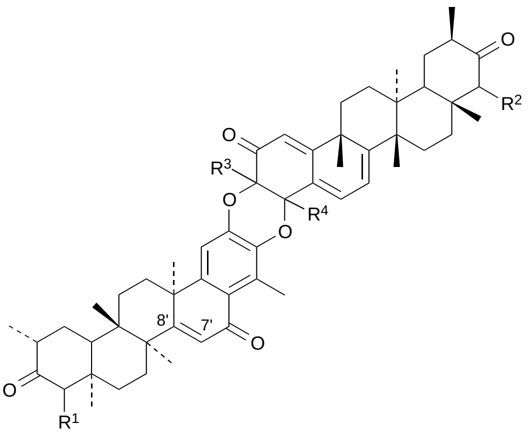


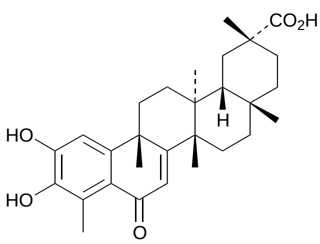
224 R = O
225 R = α-OH, H



226 R = H
227 R = OH



228 $R^1 = R^2 = H$; R^3= β-OH; R^4 = β-CH_3
229 $R^1 = R^2 = H$; R^3 = α-OH; R^4 = α-CH_3
230 R^1 = α-OH; R^2 = β-OH; R^3 = β-OH; R^4 = β-CH_3
231 R^1 = α-OH; R^2 = β-OH; R^3 = α-OH; R^4 = α-CH_3
232 $R^1 = H$; R^2 = β-OH; R^3 = β-OH; R^4 = β-CH_3
233 $R^1 = H$; R^2 = β-OH; R^3 = α-OH; R^4 = α-CH_3
234 R^1 = α-OH; $R^2 = H$; R^3 = β-OH; R^4 = β-CH_3
235 R^1 = α-OH; $R^2 = H$; R^3 = α-OH; R^4 = α-CH_3
236 $R^1 = R^2 = H$; R^3 = α-OH; R^4 = α-CH_3; 7',8'-dihydro



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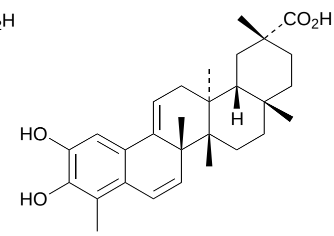
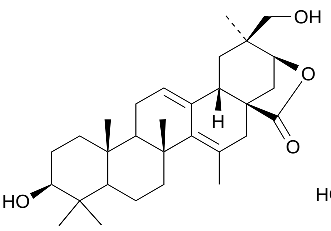


238

and wilforol B **238**, the acid from isopristimerin III, have been isolated from *Tripterygium wilfordii*.[212] The X-ray analysis of 7β,8β-epoxyfriedelin has been published.[213] 7β,8β-Epoxyfriedelin was derived from putranjivadione (friedelane-3,7-dione).

Pachanol A **239**, B **240** and C **241** are pachanane derivatives from *Trichocereus pachanoi*.[113] The structure of pachanol A **239** was confirmed by X-ray analysis. Ixerenol **242** is a rearranged oleanane from *Ixeris chinensis*.[214] Full ^{1}H and ^{13}C NMR



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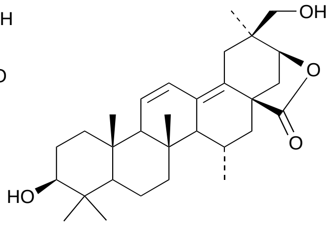

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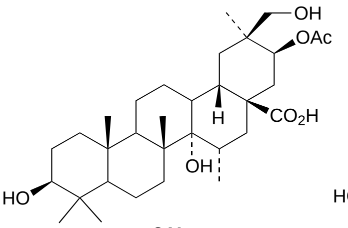

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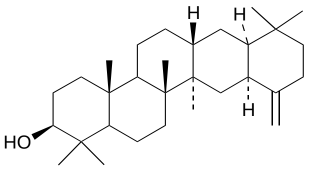


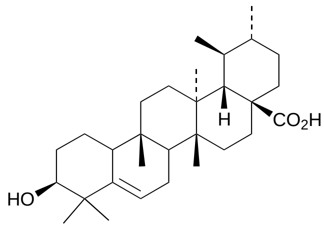
242

assignments of olean-18-ene, olean-13(18)-ene, olean-12-ene, taraxer-14-ene, multiflor-7-ene, multiflor-9(11)-ene, friedel-3-ene and friedelin have been reported.[215]

7 The ursane group

The structure of uncaric acid from *Uncaria thwaitesii* and *U. elliptica* has been revised to 3β,6β,19-trihydroxyurs-12-en-28-oic acid **243**.[216] It was formerly thought to be 3β,6β,18β-trihydroxyurs-12-en-30-oic acid. The structure of the 3β,6β-diacetate and the 3,6-diketone must also be revised. A sapogenin from *Rubus pinfaensis* has been shown to be 2α,3β,23-trihydroxyursa-12,18-dien-28-oic acid **244** by X-ray analysis of its triacetate methyl ester.[217] Two similar dienes, uncargenins A **245** and B **246** have been isolated from *U. rhynchophylla*.[218] They were accompanied by 3β,6β,23-trihydroxyolean-12-en-28-oic acid (uncargenin C) which has been isolated previously.[219] Two C-3 epimeric ursa-12,19-dienes **247** and **248** have been found in *Rosa taiwanensis*.[220] 3β-Hydroxy-18-ursen-27-oic acid **249** occurs in *Adenocalymma alliaceum*.[221]

Rhoiptelic acid **250** is a rearranged ursane from *Rhoiptelea chiliantha*.[222] Two lactone derivatives **251** and **252** have been isolated from *Bursera delpechiana*.[223] The deacetyl derivative of **251** is a known compound.[224] Other new ursanes include 2α,3α-dihydroxyurs-12-en-24-oic acid **253** and urs-12-ene-3α,24-diol **254** from *Boswellia serrata*,[225] urs-12-ene-2β,3β,22α-triol **255** and urs-12-ene-2β,3β,28-triol **256** from *Picris hieracioides*,[118] grahamidiol **257** from *Pristimera grahamii*,[226] camarinic acid **258**[125] and camaracinic acid **259**[124] from *Lantana camara*, *cis*-karenin **260** and *trans*-karenin **261** from *Nerium oleander*,[227] and 18α-ursolic acid, named as morinoursolic acid B **262**, from *Morina longifolia* together



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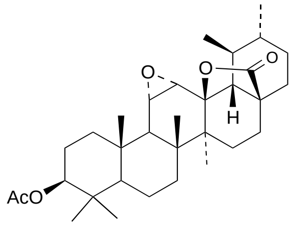

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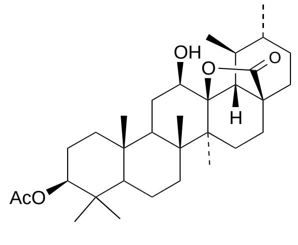

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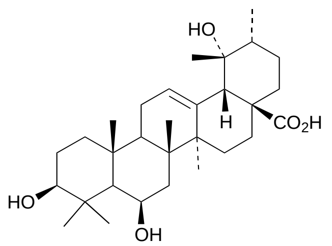

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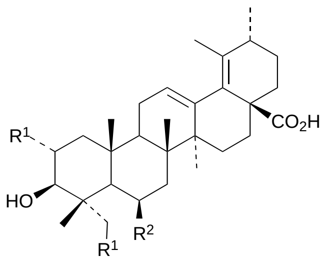
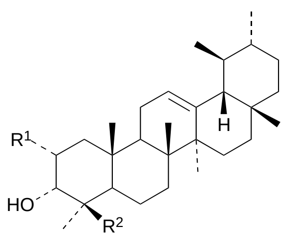
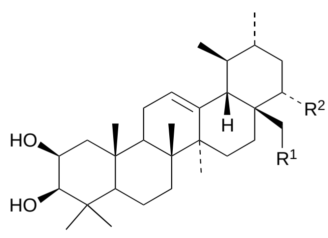


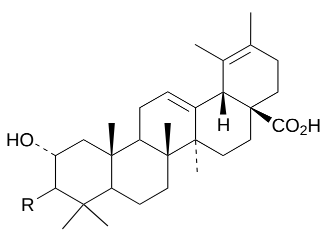
244 R^1 = OH; R^2 = H
245 R^1 = H; R^2 = OH
246 R^1 = R^2 = H; 5,6-didehydro



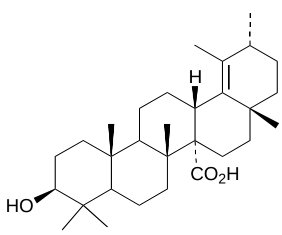
253 R^1 = OH; R^2 = CO_2H
254 R^1 = H; R^2 = CH_2OH



255 R^1 = H; R^2 = OH
256 R^1 = OH; R^2 = H



247 R = α-OH
248 R = β-OH



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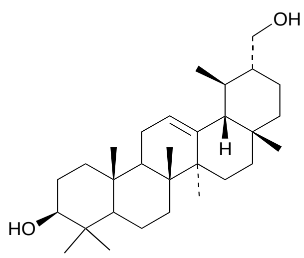

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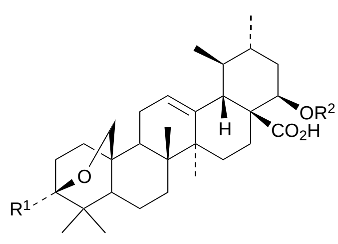
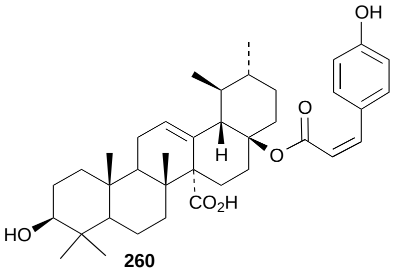
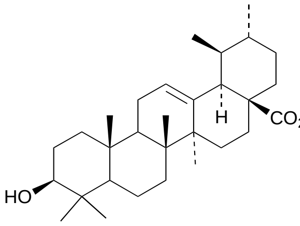


258 R^1 = OH; R^2 = Ac
259 R^1 = OMe; R^2 = angeloyl



260
261 *trans*-isomer



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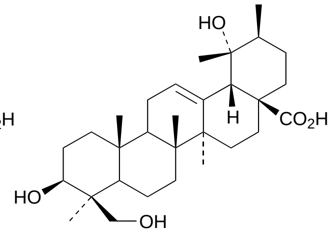


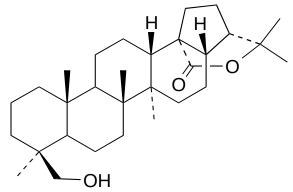
263

with the known 3-*epi*-ursolic acid, named as morinoursolic acid A.[228]

The genin of the main saponin ILA-1 of the leaves of *Ilex argentina* is claimed to be (20*S*)-3β,19α,24-trihydroxyurs-12-en-28-oic acid **263**.[229] Ursane saponins have been reported from *Adina rubella* (rubellosides A and B),[230] *Blumea lacera*,[231] *Ilex paraguariensis*,[232] *Majorana hortensis*,[233] *Mazus miquelii* (mazusaponins II and IV),[166] *Mussaenda pubescens* (Mussaendoside R),[170] *Nauclea idierrichii*,[234] *Prunella vulgaris* (pruvulosides A and B)[235] and *Zygophyllum coccineum*, *Z. album* and *Z. dumosum* (zygophyloside F).[236]

8 The hopane group

Diplaziosides I and II are hopane saponins from *Diplazium subsinuatum*.[237] The former has a new genin, 24-hydroxyhopan-28,22-olide **264**. Hopane-20α,22-diol **265** occurs in *Cyathia lepifera*[238] together with 9α,11α-epoxyfernene **266**, the corresponding 9β,11β-epoxide and 3α,10α-epoxyfilic-4(23)-ene **267**. A highly oxygenated fern-7-ene derivative, polytolypin **268**, has been obtained from the coprophilous fungus *Polytolypa hystricis*.[239]



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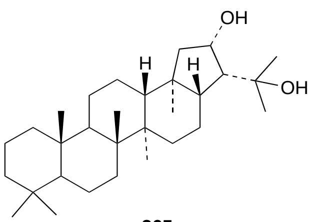

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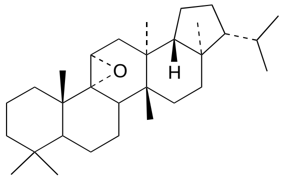

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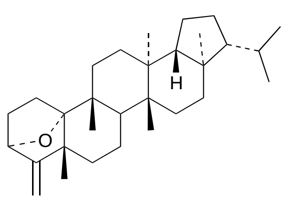

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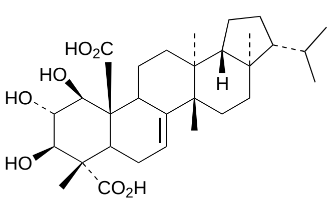

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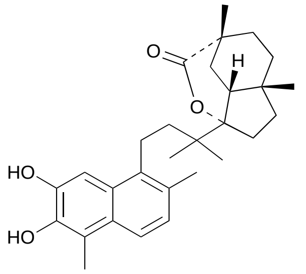
9 Miscellaneous compounds

Tryptolactone **269** is an unusual C_{27} compound from *Trypterigium wilfordii*.[240] Sodwanones G **270**, H **271** and I **272**, new members of the fascinating sipholane group of triterpenoids, have been reported from *Axinella weltneri*.[241] The structure of sodwanone G **270** was confirmed by X-ray analysis, as were the structures of the previously reported sodwanones E and F. Three new compounds of the iridal group, irisgermanicals A **273**, B **274** and C **275**, have been isolated from *Iris germanica*.[242]



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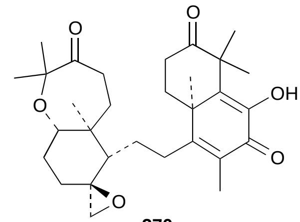

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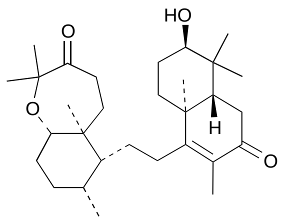

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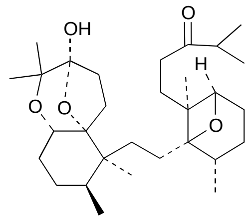

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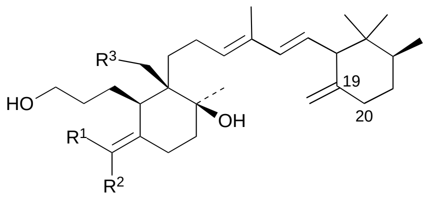
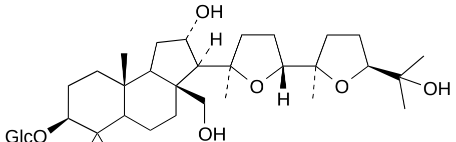


273 R^1 = CHO; R^2 = CH_3; R^3 = H
274 R^1 = CH_3; R^2 = CHO; R^3 = OH
275 R^1 = CH_3; R^2 = CHO; R^3 = OH; Δ^{19}

Adesmia aconcaguensis is the source of three new malabaricanes **276**, **277** and **278**.[243] A new shionane,



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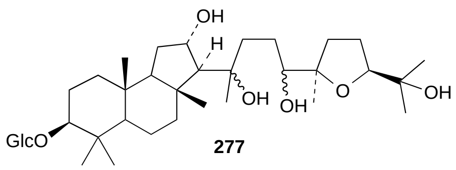

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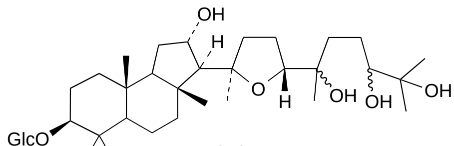

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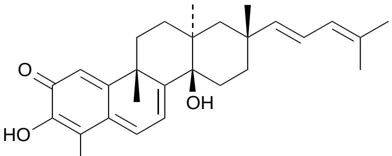
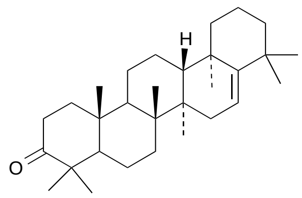


279

russulaflavidin **279**, has been found in the fungus *Russula flavida*.[244]

Picris hieracioides subsp. *japonicum* contains several 16-gammacerene and pichierene derivatives.[245] The ketone **280** is the only new gammacerene, the others having been previously described in 1989.[246] Pichierenone **281** and



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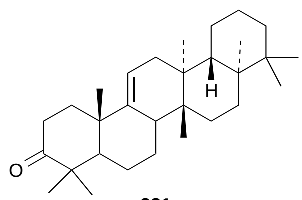
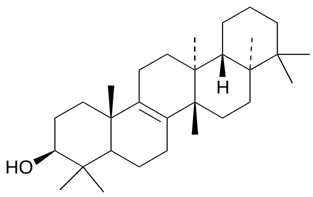
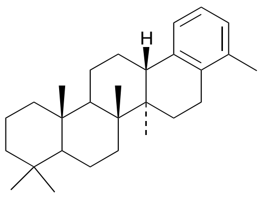


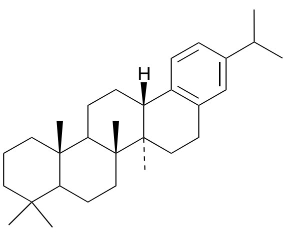
281



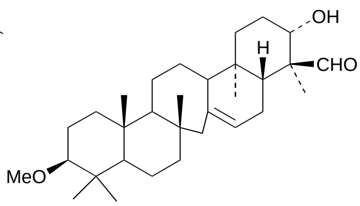
282



283



284



285

isopichierenol **282** are also new although isopichierenyl acetate has been isolated previously. Some of the ^{13}C NMR spectroscopic assignments of members of both series have been modified. The ring D aromatic gammacerane derivatives **283** and **284** have been reported from Messel shale.[247] The serratene aldehyde **285** has been found in *Picea jezoensis*.[248]

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